

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
3 July 2003 (03.07.2003)

(10) International Publication Number
WO 03/054364 A2

PCT

(51) International Patent Classification⁷: F01N 3/035,
3/20, 3/023, B01D 53/94, 53/90

(21) International Application Number: PCT/GB02/05839

(22) International Filing Date:
20 December 2002 (20.12.2002)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
0130474.0 20 December 2001 (20.12.2001) GB
0206888.0 25 March 2002 (25.03.2002) GB

(71) Applicant (for all designated States except US): JOHN-
SON MATTHEY PUBLIC LIMITED COMPANY
[GB/GB]; 2-4 Cockspur Street, Trafalgar Square, London
SW1 5BQ (GB).

(72) Inventors; and

(75) Inventors/Applicants (for US only): BLAKEMAN,
Philip, Gerald [GB/GB]; 11 Argyle Street, Cambridge
CB1 3LR (GB). TWIGG, Martin, Vincent [GB/GB];

108 Ermine Street, Caxton, Cambridge CB3 8PQ (GB).
WALKER, Andrew, Peter [GB/GB]; 57 Bramley Av-
enue, Melbourn, Royston SG8 6GB (GB). GOLUNSKI,
Stanislaw, Edmund [GB/GB]; 2 Widmore Lane, Sonning
Common, Reading RG4 9RR (GB). CHANDLER, Guy,
Richard [GB/GB]; 48 Harlton Road, Little Eversden,
Cambridge CB3 7HB (GB).

(74) Agent: NUNN, Andrew, Dominic; Johnson Matthey
Technology Centre, Blounts Court, Sonning Common,
Reading RG4 9NH (GB).

(81) Designated States (national): JP, US, ZA.

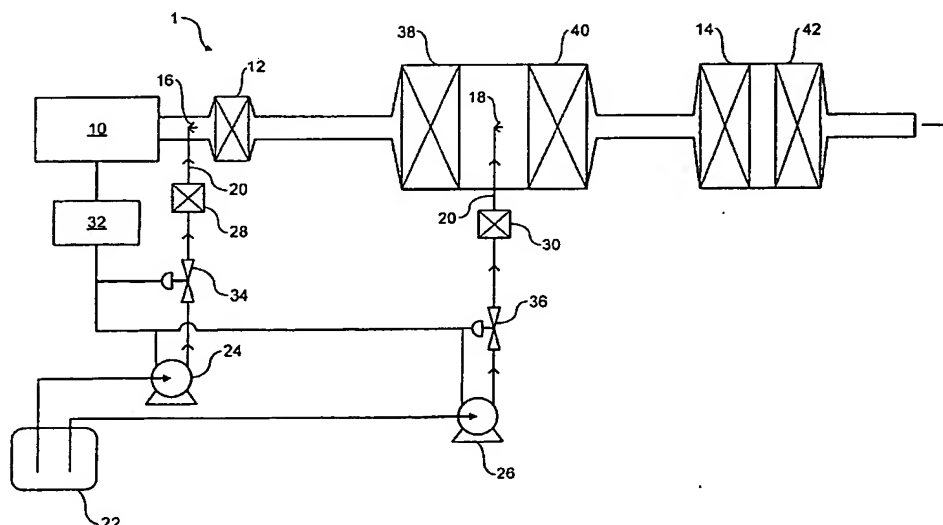
(84) Designated States (regional): European patent (AT, BE,
BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, IE, IT,
LU, MC, NL, PT, SE, SI, SK, TR).

Published:

— without international search report and to be republished
upon receipt of that report

For two-letter codes and other abbreviations, refer to the "Guid-
ance Notes on Codes and Abbreviations" appearing at the begin-
ning of each regular issue of the PCT Gazette.

(54) Title: IMPROVEMENTS IN SELECTIVE CATALYTIC REDUCTION



(57) Abstract: A method of selectively catalysing the reduction of NO_x in an exhaust gas flowing in an exhaust system of an internal combustion engine comprising a filter (40) for particulate matter comprising a second catalyst capable of selectively catalysing the reduction of NO_x with a reducing agent, which method comprising introducing a reducing agent, or a precursor thereof, into the exhaust gas and contacting the resulting gas with the filter (40).

WO 03/054364 A2

IMPROVEMENTS IN SELECTIVE CATALYTIC REDUCTION

5 The present invention relates to improvements in selective catalytic reduction (SCR) of nitrogen oxides (NO_x) in exhaust gas from internal combustion (IC) engines using a reducing agent, and in particular it relates to the use of SCR technology to treat NO_x at relatively low temperatures e.g. following cold-start. The reducing agent can be a NO_x specific reactant.

10 By "NO_x specific reactant" we mean a reducing agent that, in most exhaust gas conditions, preferentially reduces NO_x over other exhaust gas components. Examples of NO_x -specific reactants include nitrogenous compounds such as nitrogen hydrides, e.g. ammonia or hydrazine, or an ammonia precursor.

15 The ammonia can be in anhydrous form or as an aqueous solution, for example.

By "ammonia precursor" we mean one or more compounds from which ammonia can be derived, e.g. by hydrolysis. These include urea (CO(NH₂)₂) as an aqueous solution or as a solid or ammonium carbamate (NH₂COONH₄). If the urea is used as an
20 aqueous solution, a eutectic mixture, e.g. a 32.5% NH₃ (aq) is preferred. Additives can be included in the aqueous solutions to reduce the crystallisation temperature.

Urea hydrolyses at temperatures above 160°C according to equation (1) to liberate NH₃ itself. It also thermally decomposes at this temperature and above according
25 to equations (2) and (3) resulting in reduction of NO_x.



30

The application of NH₃ SCR technology to treat NO_x emissions from IC engines, particularly lean-burn IC engines, is well known. Several chemical reactions occur in the NH₃ SCR system, all of which represent desirable reactions which reduce NO_x to elemental nitrogen. The dominant reaction mechanism is represented in equation (4).



Competing, non-selective reactions with oxygen can produce secondary emissions or may unproductively consume ammonia. One such non-selective reaction is
5 the complete oxidation of ammonia, represented in equation (5).



Vehicle manufacturers are interested in adopting NH_3 SCR technology as a viable
10 means of reducing emissions of NO_x from IC engines to meet future limits on NO_x
emissions e.g. Euro 4 and Euro IV, both due in 2005 (for some heavier light commercial
vehicles Euro 4 is due in 2006). One problem associated with NH_3 SCR technology is to
maintain good NO_x conversion when the exhaust gas temperature is relatively low, e.g.
during extended idling or following cold-start. NO_x conversion can be achieved using
15 NH_3 at temperatures as low as 150°C using Pt-based catalysts, but the preferred delivery
form of ammonia, aqueous urea solution, does not decompose significantly below 200°C .
Pt-based catalysts generate nitrous oxide (NO) according to equation (5) at above about
 225°C .

20 Changes in engine test cycles have been introduced in the present Euro III
standard and will govern Euro IV type approval of new vehicles. In particular, the new
test cycles include the European Stationary Cycle (ESC); the European Transient Cycle
(ETC); and a test for smoke opacity on the European Load Response (ELR) test. These
cycles and tests include significant periods at low temperature. To attain type approval, a
25 new vehicle will have to pass both the ETC and ESC/ELR tests.

Presently, urea is the preferred source of ammonia for mobile applications
because it is less toxic than ammonia, it is easy to transport and handle, is inexpensive
and commonly available.

30

Early methods of using urea as a source of ammonia in exhaust systems involved
injecting urea directly into the exhaust gas, optionally over an in-line hydrolysis catalyst

(see EP-A-0487886 (incorporated herein by reference)). However, not all urea is hydrolysed in such arrangements, particularly at lower temperatures.

Incomplete hydrolysis of urea can lead to increased PM emissions on tests for meeting the relevant emission test cycle because partially hydrolysed urea solids or droplets will be trapped by the filter paper used in the legislative test for PM and counted as PM mass. Furthermore, the release of certain products of incomplete urea hydrolysis, such as cyanuric acid, is environmentally undesirable. Another method is to use a pre-injection hydrolysis reactor (see US-A-5,968,464 (incorporated herein by reference)) held at a temperature above that at which urea hydrolyses.

It can be seen that there remains a need for technology to improve the treatment of NO_x in exhaust gases from IC engines at relatively low temperatures. The present invention comprises a number of improvements to the SCR art and in particular to the use of SCR technology to treat NO_x at relatively low temperatures, e.g. following cold-start.

It will be appreciated that at lower temperatures, below about 100-200°C, ammonia can also react with NO₂ to produce explosive ammonium nitrate (NH₄NO₃) according to equation (6):



For the avoidance of doubt, the present invention does not embrace such reactions or the promotion of conditions which bring them about. For example, the reaction can be avoided by ensuring that the temperature does not fall below about 200°C or by supplying into a gas stream less than the precise amount of NH₃ necessary for the stoichiometric reaction with NO_x (1 to 1 mole ratio). For cold start applications, measures to prevent water from contacting the catalyst while an engine is switched off can be adopted. These can include disposing a water trap, e.g. a zeolite, upstream of the catalyst to reduce the amount of water vapour contacting the catalyst until it is heated sufficiently. A water trap can also be positioned downstream of the catalyst, to prevent atmospheric humid air from travelling up the exhaust pipe. An electric heater can also be employed to drive off moisture from the catalyst pre-cold start. Such arrangements are described in our EP 0747581, incorporated herein by reference.

In our WO 01/96717 (incorporated herein by reference), we describe an exhaust system comprising a reactor for treating an exhaust gas, which reactor comprising an oxidation catalyst, an optionally catalysed filter downstream of the oxidation catalyst, a NO_x absorbent or SCR catalyst downstream of the filter and a NO_x reduction section downstream of the absorbent or SCR catalyst. Where catalysed, the filter can comprise La/Cs/V₂O₅ or Pt/MgO. The substrate supporting the oxidation catalyst can include a region that is substantially free of catalyst and the exhaust system can comprise means for supplying a reactant upstream of the oxidation catalyst such that the reactant flowing over the region can pass to downstream components without being oxidised by the oxidation catalyst. The reactant can be a NO_x-specific reactant, especially a nitrogen hydride such as ammonia or hydrazine.

EP-A-0341382 or US-A-4,902,487 (both incorporated herein by reference) describe a method of treating diesel exhaust gas including PM and NO_x unfiltered over an oxidation catalyst to convert NO to NO₂, collecting the PM on a filter downstream of the oxidation catalyst and combusting trapped PM in the NO₂. This technology is commercially available as Johnson Matthey's CRT[®]. Further steps can be added downstream of the filter. For example a NO_x removal step including injection of a NO_x-specific reactant (as defined above) and contacting gas leaving the filter with an SCR catalyst (see our WO 00/21647 (incorporated herein by reference)).

EP-A-0283913 (incorporated herein by reference) describes a process and apparatus to remove NO_x from a gas stream. The process is characterised by passing the gas stream through a first catalytic zone in the absence of added ammonia and in the presence of an oxidation catalyst to convert the NO content thereof to NO₂, thereafter introducing ammonia into the gas stream, and catalytically reducing the NO₂ to nitrogen and water in the presence of a catalyst. The catalysts are carried on flow-through monoliths.

In our WO 99/39809 (incorporated herein by reference) we describe a SCR system for treating combustion exhaust gas containing NO_x and particulates, comprising in combination and in order, an oxidation catalyst effective to convert at least a portion of NO in the NO_x to NO₂ and enhance the NO₂ content of the exhaust gas, a particulate trap, a source of reductant fluid, injection means for the reductant fluid located

downstream of the particulate trap and an SCR catalyst. Such an arrangement is marketed by Johnson Matthey as its SCRT™.

In our WO 00/74823 (incorporated herein by reference) we describe a method of treating exhaust gas, especially from diesel engines producing low quantities of NO_x, which method comprising a first step in which hydrocarbon in the exhaust gas is oxidised, producing CO₂ and H₂O, and a second step in which soot is combusted by reaction with NO₂. The method is characterised by the oxidation of ammonia (or a precursor thereof) to form NO_x, and the introduction of the thus formed NO_x into the exhaust gas before the performance of the second step.

In our WO 99/55446 (the entire content of which is incorporated herein by reference), we describe an exhaust system including a SCR catalyst wherein ammonia or a precursor is supplied intermittently so that it is adsorbed and desorbed during the engine operating cycle.

EP 0773354 describes generating NH₃ in situ over a three-way catalyst comprising precious metals (such as Pd, Pt and Rh) carried on a layer of, for example, alumina, during rich running conditions. The NH₃ is adsorbed on a catalyst such as Cu-zeolite and is available to reduce NO_x in lean running conditions.

US Patent No. 6,125,629 describes an exhaust system comprising a close-coupled SCR catalyst and a downstream SCR catalyst and means for selectively injecting an external reductant to the SCR catalysts when they are at catalytically active temperatures.

In a first aspect, the invention provides a method of selectively catalysing the reduction of NO_x in an exhaust gas flowing in an exhaust system of an internal combustion engine, which exhaust system comprising a filter for particulate matter, which filter comprising a second catalyst capable of selectively catalysing the reduction of NO_x with a reducing agent, which method comprising introducing a reducing agent, or a precursor thereof, into the exhaust gas and contacting the resulting gas with the filter.

According to a second aspect, the invention provides an exhaust system for an internal combustion engine, which exhaust system comprising means for introducing a reducing agent, or a precursor thereof, into an exhaust gas carried by the exhaust system and a filter for particulate matter (PM) comprising a second catalyst capable of selectively catalysing the reduction of NO_x with a reducing agent, which filter is disposed downstream of the introducing means.

In one embodiment the exhaust system further comprises a first catalyst capable of selectively catalysing the reduction of NO_x with a reducing agent disposed upstream of the filter, and wherein the reducing agent or the precursor thereof, is introduced into the exhaust gas upstream of the first catalyst.

In another embodiment, the reducing agent, or the precursor thereof, is introduced into the exhaust gas upstream of the first catalyst when the first catalyst is below a first temperature.

In a further embodiment, the reducing agent or, the precursor thereof, is introduced into the exhaust gas between the first and the second catalyst. Such addition can be controlled to occur when the second catalyst is above a second temperature.

In another embodiment, the supply of reducing agent to the first catalyst is interrupted when the first catalyst is below a third temperature.

In a further embodiment, the supply of reducing agent to the second catalyst is interrupted when the second catalyst is above a fourth temperature.

In another embodiment, the first catalyst is in the close-coupled position, i.e. positioned sufficiently close enough to the exhaust manifold to be rapidly heated by exhaust gas after switch on, thereby to reach light-off temperature of NO_x reduction, but sufficiently far away from the exhaust manifold to prevent too rapid thermal ageing. Generally "close-coupled" herein is up to about 1 metre, e.g. 50cm downstream from the exhaust manifold or turbo.

In another embodiment, the exhaust system further comprises a catalyst capable of oxidising NO to NO₂ disposed upstream of the filter. The NO oxidation catalyst is disposed downstream of the first catalyst.

5 This configuration is an improvement on the exhaust system described in our WO 99/39809 and marketed by Johnson Matthey as its SCRT™ device. The oxidation catalyst/diesel particulate filter (DPF) combination has a relatively high thermal mass, so it can take a long time for the underfloor SCR catalyst to reach the temperature at which it can be used. But in the embodiment including our SCRT™ and a close-coupled SCR
10 catalyst to deal with key-on (and low temperature) NO_x, the combined system offers significant NO_x conversion advantages over the arrangement described in WO 99/39809.

A further improvement over the SCRT™ arrangement described in our WO 99/39809 can be obtained by catalysing the filter, as described in our EP 0341832, the
15 entire contents of which are incorporated herein by reference. In addition to the filter catalysts described therein such as PGMs e.g. Pt on alumina, the filter can take the form of that described in WO 00/29726 (incorporated herein by reference). For example, it can comprise a first catalyst which comprises a first PGM; a first cerium component; and preferably a zirconium component. There can be a second catalyst in communication
20 with the first catalyst, the second catalyst can comprise a second cerium component.

A further advantage of this configuration is that the performance of the oxidation catalyst/DPF combination can sometimes be limited by the engine-out NO_x/PM ratio: if there is not enough NO_x coming out of the engine then the catalyst cannot make enough
25 NO₂ to react with the engine-out PM. But within this embodiment we can inject urea over the close-coupled SCR catalyst at higher temperatures to provide an extra source of NO_x, since when urea/ammonia react with oxygen over a Pt oxidation catalyst, NO₂ can be generated. So this close-coupled urea injector can also be used to help with the active regeneration of the DPF under certain conditions.

30

In addition, in one strategy for regenerating the DPF, the temperature of the exhaust system is raised by e.g. engine means and the NO oxidation catalyst generates NO₂ to react with the PM in the downstream DPF. At such high temperatures if an

excess of urea is injected over the close-coupled SCR catalyst this can accelerate the rate of regenerating the filter, since an increased proportion of the excess urea/ammonia may be converted into NO_2 and this NO_2 can also be used to react with PM trapped on the filter, in addition to NO_2 derived from oxidation of engine-out NO_x .

5

Another way to convert NO_x at low temperature during engine start-up conditions is to react the emitted NO_x with ammonia which has been pre-adsorbed onto e.g. a zeolite material (see US-A-5,785,937 and WO 99/55446 incorporated herein by reference). Of course, the amount of NO_x that can be converted depends upon the
10 amount of ammonia stored within the SCR catalyst: once this stored ammonia is depleted, the NO_x conversion available by reaction with stored ammonia is reduced. It is not possible to inject urea to make ammonia for storage at low temperatures e.g. 150°C , because urea does not hydrolyse significantly below about 200°C . We have now found a way of treating NO_x at cold start using e.g. the preferred reductant precursor, urea.

15

According to a further aspect according to the invention, there is provided a method of reducing NO_x in an exhaust gas flowing in an exhaust system of an internal combustion engine following cold-start, which exhaust system comprising a catalyst capable of selectively catalysing the reduction of NO_x with a reducing agent, which
20 catalyst having a light off temperature for the reaction and being capable of adsorbing the reducing agent at below the light off temperature, which method comprising contacting the catalyst with a precursor of the reducing agent after engine key-off, adsorbing the precursor, or the reducing agent derived therefrom, on the catalyst between key-off and start up and reducing NO_x in exhaust gas contacting the catalyst following
25 start up.

According to a further aspect, there is provided an exhaust system for an internal combustion engine, which system comprising a catalyst capable of selectively catalysing the reduction of NO_x with a reducing agent, which catalyst having a light off temperature
30 for the reaction and being capable of adsorbing the reducing agent or a precursor thereof at below the light off temperature and means for contacting the catalyst with a precursor of the reducing agent after key-off whereby the precursor, or the reducing agent derived therefrom, is capable of adsorbing on the catalyst between key-off and start up.

In one embodiment of this aspect of the invention, the system comprises means for controlling the supply of the precursor to the catalyst. Such control means can include a suitably programmed engine control unit (ECU) or engine management unit including
5 a microprocessor or chip which, in use, controls the supply of the precursor to the catalyst.

An advantage of this arrangement is that the exhaust system is already hot enough to hydrolyse e.g. the urea at key-off, and since the engine has stopped, there is no
10 NO_x for the ammonia (generated by e.g. hydrolysis of urea or ammonium carbamate) to react with. So the ammonia can be stored on the catalyst ready for the next key-on.

Suitable catalysts for this aspect of the invention comprise zeolites, such as ZSM-5, mordenite, gamma zeolite and beta zeolite or mixtures of any two or more thereof.
15 The zeolite can be metallised or non-metallised e.g. with Fe, V, Cu, Ce, Fe or Pt or any two or more thereof. Where metallised, the metal can be applied using known techniques such as impregnation or ion-exchange.

In another embodiment, a single zeolite material is used both to adsorb and
20 desorb precursor and ammonia and to catalyse the reduction of NO_x. In another embodiment the catalyst contains a mixture, of a non-metallised zeolite, e.g. ZSM-5, to adsorb and desorb the precursor and ammonia, and a metallised zeolite e.g. Cu/ZSM-5 to catalyse the reduction of NO_x. In this last embodiment, the metallised and non-metallised zeolite can be mixed or the non-metallised zeolite can be disposed on the upstream side
25 to the metallised zeolite.

In a further embodiment, the SCR catalyst is disposed on the downstream end of the filter. This arrangement has the advantage that PM is combusted in NO₂ on the upstream part of the filter, and NO_x remaining in the gas following combustion can be
30 reduced over the catalyst downstream.

As mentioned above, it is known from US-A-5,968,464 to use a heated pre-injection hydrolysis reactor to hydrolyse urea to produce ammonia. However, according

to a further aspect of the invention, we have discovered that it is possible to generate ammonia and partially reduced nitrogen species by catalysing the reaction of some of the primary fuel, e.g. diesel, with a lean-exhaust gas. The ammonia and partially reduced nitrogen species generated can then be used to reduce the remaining NO_x in the exhaust gas.

Catalysts suitable for this reaction are known as reforming catalysts, illustrative examples of which include catalysts based on PGMs and nickel (Ni). For further details, reference can be made to D.L. Trimm and Z.I. Onsan in *Catalysis Reviews - Science and Engineering*, vol. 43 (2001) pp 31-84, the entire contents of which is incorporated herein by reference.

Further suitable reforming catalysts with utility according to this aspect of the invention include up to 2wt%, e.g. 1wt%, rhodium dispersed on a refractory oxide support material which comprises cations of cerium and zirconium - see our WO 99/48805, the entire contents of which is included herein by reference. In addition to the supported up to 2wt% Rh, such as up to 1wt% Rh, other catalysts include low loadings of Pt (up to 0.5wt%, e.g. 0.1 wt%) and Rh-Pt comprising up to 2wt% Rh (e.g. up to 1wt% Rh) and up to 0.5wt% Pt (e.g. up to 0.1wt%). Supports for the Rh, Pt, Rh-Pt and Ni include alumina, titania, ceria, zirconia, silica, silica-alumina and mixtures and mixed oxides containing any two or more thereof.

Therefore, according to a further aspect, the invention provides a method of making ammonia and/or partially reduced nitrogen species for reducing NO_x in an exhaust gas of a lean burn internal combustion engine, which method comprising passing a hydrocarbon and a lean exhaust gas over a reforming catalyst.

By "partially reduced nitrogen species" herein we include nitriles, amines, oximes and isocyanates.

The gas composition generated over the reforming catalyst containing ammonia and/or partially reduced nitrogen species can be referred to as a "reformate".

According to a further aspect, the invention provides an exhaust system for a lean burn internal combustion engine which system comprising means for contacting a reforming catalyst with a hydrocarbon, means for contacting the reforming catalyst with at least a portion of a lean exhaust gas exhausted from an engine thereby to generate a reformat comprising ammonia and/or partially reduced nitrogen species with the hydrocarbon, a catalyst for selectively catalysing the reduction of NO_x with a reducing agent, and means for contacting the SCR catalyst with the reformat.

In one illustrative example, the hydrocarbon is the fuel that powers the engine. The lean burn engine can be any engine that produces a lean exhaust gas. For example, it can be a gasoline engine, such as a gasoline direct injection engine, or a diesel engine. Alternatively, it can be powered using non-typical fuels, such as natural gas, methanol and liquid petroleum gas.

In a further illustrative embodiment, the exhaust gas is carried in an exhaust conduit and the reforming catalyst is disposed in the conduit, the means for contacting the reforming catalyst with a hydrocarbon is an injector disposed upstream of the reforming catalyst.

In a further illustrative embodiment, a portion of the exhaust gas is removed from the exhaust gas stream and directed to the reforming catalyst. The resulting reformat containing NH_3 or related species can be fed back into a conduit carrying the remaining exhaust gas and over the SCR catalyst. In a preferred arrangement according to this embodiment, the exhaust system comprises the SCRT™ system described in WO 99/39809, wherein a portion of the exhaust gas stream is removed from upstream of the CRT® unit, and the reformat containing NH_3 or related species is injected downstream of the CRT® unit, but upstream of the SCR catalyst.

The SCR catalysts for use in the present invention can be any known to the person skilled in the art. However, the first, second, third and fourth temperatures may depend on the nature of the catalyst and accordingly the introduction of reducing agent injected into the system as pre-programmed into the control means. A catalyst can be chosen according to the conditions it is expected to encounter e.g. temperature range of

operation, exhaust gas composition, and the duty it is to perform e.g. the percentage NO_x conversion. Such parameters can be assessed using exhaust system modelling techniques known in the art. Of course, a catalyst can be chosen according to its propensity to oxidise ammonia to NO at a particular temperature for the performance of exhaust
5 treatment processes further downstream.

For example, Pt-based SCR catalysts can catalyse the reduction of NO_x with ammonia at between about 175°C and about 250°C. Above about 250°C the oxidation of ammonia to NO predominates, thus losing its selectivity. Medium temperature
10 vanadium-based catalysts, e.g. $\text{V}_2\text{O}_5/\text{TiO}_2$, operate in the temperature range between about 260°C and about 450°C. Again beyond about this higher temperature, selectivity is lost and NO is produced. If the exposure temperature of the $\text{V}_2\text{O}_5/\text{TiO}_2$ catalyst exceeds a certain level, the active, high surface area anatase phase of TiO_2 irreversibly converts to rutile with a surface area of less than 10 m^2/g . Normally this conversion takes place at
15 about 500°C and about 550°C, but catalysts may include stabilisers to increase their thermal durability. Some $\text{V}_2\text{O}_5/\text{TiO}_2$ catalysts have been reported to be thermally stable up to about 700°C.

Zeolites can operate in the temperature range of about 350°C to about 600°C.
20 Zeolites suitable for use in catalysts according to the present invention include ZSM-5, mordenite, gamma-zeolite or beta-zeolite. They can comprise at least one metal or be metallised with at least one metal, which metal can be selected from one or more of Cu, Ce, Fe or Pt, and they can be ion-exchanged or impregnated.

25 Zeolites are characterised by their crystalline structure and $\text{SiO}_2:\text{Al}_2\text{O}_3$ ratio. For example, common mordenites have a ratio of about 10. When NO_x is present in the exhaust gas, zeolite-based SCR catalysts do not oxidise ammonia to NO_x . Therefore, unlike Pt or V_2O_5 catalysts, its selectivity towards NO_x conversion continually increases with temperature. However, zeolite-based catalysts can have stability problems when
30 exposed to high temperatures in the presence of water vapour. At exposure temperatures above 600°C, in a high water content process stream, zeolites tend to deactivate by dealumination whereby Al^{3+} ion in the $\text{SiO}_2\text{-Al}_2\text{O}_3$ framework migrates out of the structure.

This leads to permanent deactivation and, in extreme cases, collapse of the crystalline structure.

Of course, zeolites are preferred where adsorption of ammonia on a catalyst is
5 required, see WO 99/55446.

The exhaust systems for the present invention are for IC engines and in particular to lean-burn IC engines. These can include gasoline lean-burn engines, such as gasoline direct injection (GDI) engines. It can also include diesel engines. In particular, diesel
10 engines can include heavy-duty diesel engines (as defined in Europe by European Directives 88/77/EEC and 1999/96/EC). In the USA, heavy-duty vehicles are defined by gross vehicle weight rating (GVWR) 8,500 lbs in the US Federal jurisdiction and above 14,000 lbs in California (model year 1995 and later). The heavy-duty diesel category is subdivided into light heavy-duty diesel engines: $<8,500 \text{ lbs} < \text{LHDDE} < 19,500 \text{ lbs}$ (14,000
15 $\text{lbs} < \text{LHDDE} < 19,500$ in California, 1995+); medium heavy-duty diesel engines: $19,500 \text{ lbs} < \text{MHDDE} < 33,000 \text{ lbs}$; and heavy heavy-duty diesel engines (including urban buses): $\text{HHDE} > 33,000 \text{ lbs}$. Diesel engines can also be light-duty diesel engines as defined in Europe by European Directive 70/220/EEC, as amended by 93/59/EC and 98/69/EC. In the USA passenger vehicles, light light-duty trucks (LLDT), below 6000 lbs GVWR and
20 heavy light-duty trucks (HLDT), above 6000 lbs are included in the light-duty diesel category.

In order that the invention may be more fully understood, embodiments of the invention are described with reference to the accompanying drawings, in which:

Figure 1 is a schematic diagram of an exhaust system for a diesel engine
25 including a close-coupled SCR catalyst and an underfloor SCR catalyst;

Figure 2 is a further embodiment of the exhaust system according to the invention shown in Figure 1;

Figures 3A, 3B and 3C are schematic diagrams of exhaust systems for a lean burn engine including a reforming catalyst for generating a reformat from lean-burn exhaust
30 gas and a hydrocarbon fuel;

Figure 4 is a graph showing the % NO_x Conversion against % ammonia:NO_x ratio for an exhaust system comprising 10g/ft³ Pt catalyst for oxidising NO in a synthetic diesel feed gas to NO₂ and a V₂O₅/TiO₂ SCR catalyst coated on a downstream DPF. The system further comprises an injection means for introducing ammonia into the exhaust gas downstream of the oxidation catalyst. Measurements were taken at 350°C;

Figure 5 is a graph illustrating light-off temperature for a SCRTTM system compared with a SCRTTM system including a close-coupled SCR catalyst;

Figure 6 is a graph illustrating time to light-off (in seconds) for the systems in Figure 5;

Figure 7 is a graph showing the amount of stored ammonia available for the SCR reaction on an SCR catalyst; and

Figure 8 is a graph showing H₂ or NH₃ detected against temperature for a 1wt% Rh/Ce-Zr hydrocarbon reforming catalyst in a synthetic exhaust gas mixture.

Figure 1 is a schematic diagram of an exhaust system 1 for a diesel engine 10. The exhaust system 1 comprises a first SCR catalyst 12 in the close-coupled position and a second SCR catalyst 14 in the underfloor position. A first injection means 16 for introducing ammonia into an exhaust gas carried in the exhaust system 1 is disposed in the exhaust system 1 upstream of the first SCR catalyst 12. A second injection means 18 for introducing ammonia into an exhaust gas is disposed in the exhaust system 1 upstream of the second SCR catalyst 14 and downstream of the first SCR catalyst 12.

In the embodiment illustrated, ammonia is generated by hydrolysing an aqueous urea solution. The urea solution is stored in an optionally replaceable tank 22. Urea is drawn from the tank by pumps 24, 26 and conducted to optionally heated, e.g. to about 300°C, hydrolysis catalysts 28, 30. Ammonia liberated from the hydrolysis is conducted to the relevant injection means 16, 18 via tubing 20. Supply of the urea to the hydrolysis catalysts 28, 30 is controlled by valves 34, 36 which are in turn controlled by control unit 32, as are pumps 24, 26. Control unit 32 can include a pre-programmed microchip means, for example.

Control unit 32 receives signals from sensors (not shown) in the exhaust system and can adjust the flow of ammonia to the injections means 16, 18 accordingly. According to the present invention, ammonia is supplied to the inlet of the first catalyst when the first catalyst is below a first temperature e.g. about 275°C, and ammonia is
5 supplied to the inlet of the second catalyst when the second catalyst is above a second temperature, e.g. about 175°C.

The illustrated embodiment includes a catalyst 38 for oxidising NO in an exhaust gas to NO₂. Such a catalyst can be a Pt/Al₂O₃ catalyst. The illustrated system also
10 includes a DPF 40 comprising an SCR catalyst disposed downstream of the second injection means 18.

In the embodiment illustrated, ammonia can be introduced into the exhaust gas via first injection means 16 when the first catalyst reaches about 150°C (referred to
15 herein as the third temperature), e.g. following cold-start. NO_x generated by the diesel engine 10 is reduced over the first SCR catalyst 12 to prevent it being exhausted to atmosphere. The supply of ammonia can be suspended when the first SCR catalyst 12 reaches a first temperature, e.g. about 200°C.

20 As the exhaust system heats up, the second catalyst 14 becomes sufficiently hot to catalyse the reduction of NO_x and so ammonia is supplied to the second injection means 18. The temperature (referred to herein as the second temperature) of the second catalyst at which ammonia is injected via the second injection means can be higher or lower than the first temperature. In the embodiment illustrated it is about 175°C.

25 In order to avoid exhausting ammonia injected into the exhaust gas for treating NO_x to atmosphere, the exhaust system 1 illustrated can include a clean-up catalyst 42 e.g. of known formulation.

30 An exhaust system for a diesel engine, which exhaust system comprising a catalyst for oxidising NO to NO₂ disposed upstream of a DPF is described in EP-A-0341832 and US-A-4,902,487. PM trapped on the filter can be combusted in NO₂ generated upstream. A problem with this arrangement is that in certain operating

conditions there can be insufficient NO_x in the exhaust gas to increase the $\text{NO}_2:\text{NO}$ ratio thereby to combust trapped PM. Reasons for low exhaust gas NO_x levels can include: the engine temperature is too low e.g. following cold-start; the oxidation catalyst is not sufficiently hot enough to produce sufficient NO_2 ; and/or the exhaust system includes
5 means for reducing the level of NO_x in the exhaust gas e.g. exhaust gas recirculation (EGR). The embodiment illustrated according to the present invention includes at least one feature designed to meet these problems.

Control unit 32 can be programmed such that ammonia is supplied even after the
10 first catalyst rises above a temperature at which it catalyses NO_x reduction and instead leads to ammonia oxidation. In this way additional NO_x is introduced into the exhaust system and can be oxidised on the oxidation catalyst 38 thereby to produce NO_2 for combusting PM trapped on the DPF 40. The nature of the first SCR catalyst 12 can be chosen to oxidise ammonia to NO at lower temperatures where necessary. For example,
15 platinum-containing SCR catalysts generally oxidise ammonia to NO at lower temperatures, e.g. > about 250°C , than vanadium-based catalysts generally which produce NO from NH_3 at above about 450°C .

Alternatively, in the embodiment illustrated in Figure 1, the SCR catalyst
20 supported on the DPF 40 can be referred to as the second catalyst and downstream SCR catalyst 14 can be referred to as a third (or a further) SCR catalyst.

A variation of the exhaust system of Figure 1 is shown in Figure 2, with common features from Figure 1 bearing the same reference numerals. The Exhaust system of
25 Figure 2 operates in the same way as described in connection with Figure 1 except as follows.

The exhaust system in Figure 2 includes a bypass 44, 46 of hydrolysis catalysts 28 and 30 respectively. Each bypass 44, 46 is controlled by a valve 48, 50, and each
30 valve is controlled by control unit 32.

In use, the control unit 32 operates valves 48, 50 to enable urea to bypass the catalysts 28, 30. Flow of the urea to injection means 16, 18 is controlled by valves 34

and 36 during bypass operation. Operation of the bypass valves 48, 50, in the embodiment illustrated, is done immediately after key-off i.e. when SCR catalysts 12, 40 are still hot. At such temperature, urea can be hydrolysed to ammonia and the ammonia is adsorbed to the SCR catalysts 12, 40.

5

Since there is no exhaust gas flowing in the exhaust system, the adsorbed ammonia can remain adsorbed to the catalyst until key-on and is thus available to reduce NO_x at low exhaust gas temperatures following start-up.

Figures 3A, 3B and 3C are schematic diagrams of exhaust systems for a lean burn engine including a reforming catalyst for generating a reformat from lean-burn exhaust gas (represented by the bold arrow) and hydrocarbon fuel.

In the Figures, 100 is an exhaust gas conduit, 110 is a reformer and 120 is a SCR catalyst. In Figure 3A 130 is an exhaust gas conduit 100 bypass for conveying a portion of the exhaust gas to the reformer 110; 140 is a supply of either gasoline or diesel hydrocarbon fuel; and 150 is a conduit for conveying a reformat-rich gas to rejoin and mix with exhaust gas in the exhaust gas conduit 100.

In Figure 3B, 160 is a fuel injector.

In Figure 3C, 170 is a supply of diesel fuel; 180 is a catalyst for oxidising NO in the exhaust gas to NO_2 ; and 190 is a diesel particulate filter, optionally catalysed. Catalyst 180 and DPF 190 as a unit can be referred to as a CRT[®] and is described in our EP-A-0341832.

25

We believe that the arrangements illustrated are self explanatory. Figure 3C illustrates an embodiment of the invention as applied to our SCRT[™] concept as described in WO 99/39809.

The following Examples are provided by way of illustration only.

EXAMPLE 1

NO_x Conversion over Diesel Particulate Filter including SCR Catalyst

Figure 4 shows a graph of the % NO_x Conversion against % ammonia:NO_x ratio for an exhaust system comprising 10g/ft³ Pt catalyst for oxidising NO in a synthetic diesel feed gas to NO₂ and a V₂O₅/TiO₂ SCR catalyst coated on a downstream DPF. The system further comprises an injection means for introducing ammonia into the exhaust gas downstream of the oxidation catalyst. Measurements were taken at 350°C. Peak NO_x conversion is nearly 40%. Residual NH₃ injected upstream of the filter can 'slip' to a downstream SCR catalyst.

The arrangement including a further SCR catalyst downstream of the catalysed DPF is a variation on our system described in WO 99/39809 and marketed by Johnson Matthey as its SCRTTM device. Advantages of this modified arrangement include that some SCR conversion can then be obtained in the filter, meaning that the downstream SCR system (which today would typically be around 15-30 litres) could be reduced in size, because some of the NO_x conversion had already been done within the filter.

A further advantage, which can be obtained whether the filter is catalysed or not, is that the excess urea which passes through the filter will be mixed more effectively as it leaves the filter, since filters introduce turbulence at their outlets. Improved mixing gives rise to increased conversion efficiency. Furthermore, within the SCRTTM system the filter gets hot before the SCR system, since it is closer to the engine. Therefore, by injecting urea in front of the filter we would be able to inject at an earlier point in the legislative cycle than would be the case if we were injecting urea just in front of the (sole) SCR catalyst. This last advantage is another way to obtain improved cold-start NO_x performance.

EXAMPLE 2

NO_x Conversion in SCRTTM System including Close-Coupled SCR catalyst

This Example is designed to show the improvement in NO_x control following cold-start in an exhaust system including a close-coupled SCR catalyst and associated upstream ammonia injector coupled with an underfloor SCR catalyst when compared with an exhaust system including only an underfloor SCRTTM system. Whilst this Example does not include an SCR catalysed DPF, it will be appreciated that the

combined close-coupled SCR catalyst/underfloor SCR catalyst system wherein the underfloor SCR catalyst is an SCR catalysed DPF would provide yet more NO_x control, as demonstrated by the results in Example 1 above.

5 Tests were done on a bench engine including an exhaust system comprising an SCRT™ system. By "SCRT™" system we mean the system described in our WO 99/39809. Briefly, in order from upstream to downstream, it consists of a catalyst for oxidising NO in the exhaust gas to NO₂, a filter for particulate matter in the exhaust gas, means for injecting a reductant into an exhaust gas carried in the exhaust system and a
10 selective catalytic reduction catalyst. The combination of the NO oxidation catalyst and the filter, as a unit, is described herein as a CRT® and is described in more detail in our EP 0341832. The engine was a 10 litre heavy-duty turbo diesel engine configured to meet EU II legislation. Ammonia gas was injected into the exhaust as reductant. Emissions were measured using standard techniques.

15

The SCR catalyst in both the SCRT™ system and the close-coupled SCR catalyst was V₂O₅/TiO₂. All catalysts were coated on a ceramic honeycomb monolith of diameter 10.5 inches (26.67 cm) and length 6 inches (15.24cm) (volume 8.5 litres). The cell density was 400 cells per square inch (cpsi (62 cells cm⁻²) and the cell wall thickness was
20 6×10^{-3} inches (0.015cm). The CRT® filter unit consisted of a ceramic wall flow filter of diameter 10.5 inches (26.67cm) and length 12 inches (53.34cm) (volume 17 litres). The cell density was 200 cpsi and wall thickness was 0.014 inches (0.036cm).

The catalysts were mounted in the exhaust system in two configurations. The first
25 configuration was a base-line (or control) system comprising a SCRT™ system, consisting of a CRT® (oxidation catalyst + particulate filter) upstream of an ammonia injection point, and two SCR catalysts (17 litre volume) downstream of the ammonia injection point. The second configuration was the same as the base-line system described above but was expanded to include a further SCR catalyst (8.5 litres) upstream of the
30 CRT®, in a close-coupled position (about 1 metre downstream of the turbo) with another ammonia injection point upstream of the whole system, according to the invention. In the second configuration ammonia was injected only through the injector situated upstream of the close-coupled SCR catalyst and not through the SCRT™ injector. Accordingly,

the second configuration could be described as a close-coupled SCR catalyst with associated ammonia injector and underfloor SCR catalyst.

These two systems were tested for NO_x conversion over a temperature ramp
5 between 125°C and 275°C turbo out temperatures (i.e. simulating a cold start situation). The light-off activity for the SCR reaction of the two systems is shown in Figure 5. With an SCR catalyst in front of the SCRT™ system, light-off on this test procedure is achieved at 15°C lower turbo-out-temperature than with the SCRT™ system alone. This difference is even more important when the time is considered. As shown in Figure 6, the
10 light-off time over this test procedure for the SCR+SCRT™ system is about 1 minute less than for the SCRT™ system.

Thus, a close-coupled SCR catalyst can be employed to make more efficient use of the heat from the engine in cold start and/or transient situations.

15

EXAMPLE 3

NO_x Conversion in SCRT™ System with Close-Coupled SCR catalyst and Temperature Dependent Reduction Injection

20

This Example is to compare the NO_x conversion activity of first two exhaust system configurations of Example 2 with a third configuration in which ammonia was injected only via the close-coupled SCR catalyst injector during a warm-up phase (simulating cold-start or low temperature running) and then switched to injection via the
25 SCRT™ injector when the SCRT™ SCR catalyst was up to temperature. This strategy is referred to herein as a dual-injector strategy.

A dual injector strategy for ammonia is ideally required to switch the system operation back to a standard SCRT™ configuration - upstream CRT® and downstream
30 SCR - once the larger (and therefore more efficient) downstream SCR catalysts are warm enough to convert NO_x. To demonstrate this, the same ramp up procedure as described in the previous example was employed. Once 275°C was reached, the engine was run at this point for 5 minutes to ensure the heat was distributed throughout the system. The

overall NO_x conversion from this test for the SCRT™, SCR+SCRT™ and the SCR+SCRT™ with optimised ammonia injection are summarised in table 1.

Table 1: Overall NO_x conversion over a simulated cold-start test for different systems.

System	Overall NO _x conversion (%)
SCR+SCRT™ (only upstream injection)	51.7
SCRT™	54.7
SCR+SCRT™ (dual injector strategy)	58.4

It is clear that the SCR+SCRT™ system, while having advantages during warm-up (as demonstrated in the previous example), is less good over the whole test as the small close-coupled SCR catalyst cannot convert all of the NO_x from the engine. The SCRT™ system is better over this test as once the system is warm, the large SCR volume makes the NO_x conversion much more efficient. But combining the two strategies, with ammonia injection upstream of the close-coupled SCR catalyst during the ramp up, followed by a switch of the ammonia injection to downstream of the CRT® (i.e. standard SCRT™ operation), gives the best overall NO_x conversion. The system takes advantage of the fast warm-up of the close-coupled SCR and then the greater SCR volume once the downstream catalysts are warm.

EXAMPLE 4

Ammonia Storage on an SCR Catalyst

To quantify the amount of ammonia stored on an SCR catalyst, the following procedure was followed:

In a laboratory reactor, an SCR catalyst (coated on a ceramic honeycomb monolith of diameter 1 inch (2.54cm) and length 3 inches (7.62cm), with a cell density of 400 cpsi (62 cells cm⁻²) per square inch and a cell wall thickness of 6 x 10⁻³ inch (0.015cm) was exposed to gas mix A to saturate the surface with ammonia (i.e. when

inlet ammonia equals outlet ammonia). Then, gas mix B was introduced to react stored ammonia with NO_x via the SCR reaction. The amount of NO_x converted is therefore a measure the amount of stored ammonia which is available for the SCR reaction. Gas mix B was continued until NO_x conversion reached 0%.

5 GAS MIX A

	Space Velocity:	30,000 hr^{-1}
	NO:	0 ppm
	NO ₂ :	0 ppm
	SO ₂ :	0 ppm
10	NH ₃ :	200 ppm
	O ₂ :	14 %
	H ₂ O:	4.5%
	CO ₂ :	4.5%
	N ₂ :	balance

15

GAS MIX B

	Space Velocity:	30,000 hr^{-1}
	NO:	100 ppm
20	NO ₂ :	100 ppm
	SO ₂ :	0 ppm
	NH ₃ :	0 ppm
	O ₂ :	14 %
	H ₂ O:	4.5%
25	CO ₂ :	4.5%
	N ₂ :	balance

The results are shown in Figure 7. As temperature increases, the amount of NH_3 stored and available for reaction becomes less, and at low temperatures, there appears to be a saturation point at about 0.5 g NH_3 / litre of catalyst. Clearly, however, it is possible to store ammonia on an SCR catalyst and use it for subsequent reaction with NO_x .

The length of time that measurable NO_x conversion (> 10%) is achieved in this test ranges from 15 minutes at 150°C to 90 seconds at 400°C. Clearly, such times are not insignificant, and on a vehicle a reductant injection strategy which takes advantage of this phenomenon could offer advantages.

EXAMPLE 5

Formation of Ammonia using a Hydrocarbon-Reforming Catalyst)

A rhodium-containing catalyst, previously disclosed for hydrocarbon reforming by reaction with oxygen and water (WO 99/48805, Example 1), was prepared using known techniques. Briefly, a batch of catalyst with a nominal composition of 1%Rh/CeO₂-ZrO₂ (based on the proportions of precursors) was prepared by
5 impregnating 50g of 50:50 (by mass) ceria-zirconia support material with an aqueous Rh-salt solution. The required amount of impregnating solution (30cm³) was prepared by adding distilled water to 3.64g of aqueous rhodium(III) nitrate containing 0.5g rhodium.

The impregnating solution was added to the support material and mixed
10 thoroughly. Excess water was removed from the resultant paste, which was then left for 2 hours to form a semi-rigid cake. After breaking-up the cake, the lumps were dried at 120°C for 8 hours, before being calcined in static air at 500°C for 2 hours. Finally, the catalyst was crushed, pelletised (using a pressure of 8500kg cm⁻² for 15 min) and sieved to collect granules in the range 0.3-0.8mm diameter. No special activation was required
15 prior to testing.

This catalyst was then exposed to an oxygen-rich synthetic exhaust-gas (inlet stream). The catalyst was in the form of a powder, which was loosely packed into a bed (0.6 g), to which the inlet stream was fed at a rate of 2 litres per minute. The inlet stream
20 contained 1% O₂, 10% CO₂, 10% H₂O, and the balance was N₂. The gas emerging from the catalyst bed was analysed for hydrogen (using a mass spectrometer), while the inlet stream was heated from 150°C to 600°C at a rate of 5°C per minute. As the temperature approached 200°C, 1% propene was added to the inlet stream to mimic the injection of fuel into the exhaust gas. As can be seen from the graph at Figure 8, initially, no
25 hydrogen was detected. However, when the temperature reached 250°C, the hydrogen peaks in the mass spectrum began to rise.

The experiment was repeated, except that the inlet stream contained 1800 ppm NO in addition to 1% O₂, 10% CO₂, and 10% H₂O. Once again, as the temperature
30 approached 200°C, 1% propene was added. In this experiment, the gas emerging from the catalyst bed was analysed for NO_x and ammonia. The NO_x concentration began to decline as soon as the propene was added, but no ammonia was detected initially. As can be seen in the Figure, the temperature reached 250°C, ammonia formation suddenly

began to occur, and at the same time the rate of NO_x conversion increased (see figure below). Between 310°C and 370°C , the ammonia concentration in the emerging gas stabilised at 1150 ppm, corresponding to hydrogenation of 65% of the NO_x in the inlet stream. The remaining 35% of the NO_x was reduced to N_2 .

5

These experiments showed that, by using a reforming catalyst, it is possible to convert hydrocarbon and NO_x to ammonia in an exhaust gas. The onset of ammonia formation corresponds closely to the temperature at which hydrogen formation is detected when NO_x is absent. The results indicate that as soon as the reforming reactions

10 start to occur, the hydrogen formed can immediately react with NO_x to form ammonia.

CLAIMS:

1. A method of selectively catalysing the reduction of NO_x in an exhaust gas flowing in an exhaust system of an internal combustion engine, which exhaust system comprising a filter for particulate matter, which filter comprising a second catalyst capable of selectively catalysing the reduction of NO_x with a reducing agent, which method comprising introducing a reducing agent, or a precursor thereof, into the exhaust gas and contacting the resulting gas with the filter.
2. A method according to claim 1, wherein the exhaust system further comprises a first catalyst capable of selectively catalysing the reduction of NO_x with a reducing agent disposed upstream of the filter, and wherein the reducing agent, or the precursor thereof, is introduced into the exhaust gas upstream of the first catalyst.
3. A method according to claim 2, wherein the reducing agent, or the precursor thereof, is introduced into the exhaust gas upstream of the first catalyst when the first catalyst is below first temperature.
4. A method according to claim 1, 2 or 3, wherein the reducing agent, or the precursor thereof, is introduced into the exhaust gas between the first and the second catalyst.
5. A method according to claim 4, wherein the reducing agent, or the precursor thereof, is introduced into the exhaust gas between the first and the second catalyst when the second catalyst is above a second temperature.
6. A method according to claim 2 or 3, wherein the introduction of reducing agent, or the precursor, upstream of the first catalyst is interrupted when the first catalyst is below a third temperature.
7. A method according to claim 4 when appendant on claim 2 or 3 or claim 5, wherein the introduction of reducing agent, or the precursor, between the first and the second catalyst is interrupted when the second catalyst is above a fourth temperature.

8. A method according to claim 3, wherein the first temperature is from 175-600°C, preferably from 250-450°C and most preferably from 300-400°C.
9. A method according to claim 5, wherein the second temperature is from 175-600°C, preferably from 250-450°C and most preferably from 300-400°C.
10. A method according to claim 5 when appendant to claim 3, wherein the first temperature is the same as the second temperature.
11. A method according to claim 6, wherein the third temperature is from 75-200°C, preferably from 100-175°C and most preferably from 125-160°C.
12. A method according to claim 7, wherein the fourth temperature is 250-600°C, preferably 450-600°C and most preferably 600°C and above.
13. A method according to claim 3, wherein the first temperature is sufficiently high as to permit the formation of NO_x from the reducing agent, which method further comprising the step of combusting PM trapped on the filter in NO₂ in the NO_x, optionally at up to 400°C.
14. A method according to claim 4, wherein the exhaust system further comprises a catalyst for oxidising NO in the NO_x to NO₂ disposed upstream of the filter and a reducing agent supply for the second catalyst and downstream of the first catalyst, which method further comprising the step of oxidising NO in the exhaust gas to NO₂ and combusting PM trapped on the filter in the NO₂, optionally at up to 400°C.
15. A method according to any preceding claim, further comprising the step of contacting gas leaving the filter with a further catalyst capable of selectively catalysing the reduction of NO_x with a reducing agent.
16. An exhaust system for an internal combustion engine, which exhaust system comprising means for introducing a reducing agent, or a precursor thereof, into an exhaust gas carried by the exhaust system and a filter for particulate matter (PM)

comprising a second catalyst capable of selectively catalysing the reduction of NO_x with a reducing agent, which filter is disposed downstream of the introducing means.

17. An exhaust system according to claim 16, further comprising a first catalyst capable
5 of selectively catalysing the reduction of NO_x with a reducing agent wherein the
introducing means is a first introducing means and is disposed upstream of the first
catalyst.
18. An exhaust system according to claim 16 or 17, further comprising a second means
10 for introducing a reducing agent into the exhaust gas between the first catalyst and
the second catalyst.
19. An exhaust system according to claim 16, 17 or 18, further comprising means for
controlling the introduction of reducing agent, or a precursor thereof, into the exhaust
15 gas through the or each introducing means during a drive cycle thereby to reduce the
amount of NO_x in the gas exhausted atmosphere.
20. An exhaust system according to claim 17, wherein the first catalyst is in the close-
coupled position relative to an engine.
20
21. An exhaust system according to any of claims 16 to 20, wherein the second catalyst
is in the underfloor position.
22. An exhaust system according to claim 19, wherein the control means, in use, causes
25 the introduction of reducing agent into the exhaust gas through the first introducing
means when the first catalyst is below a first temperature.
23. An exhaust system according to claim 22, wherein the first temperature is from 175-
600°C, preferably from 250-450°C and most preferably from 300-400°C.
30
24. An exhaust system according to claim 19, wherein the control means, in use, causes
the introduction of reducing agent into the exhaust gas through the second
introducing means when the second catalyst is above a second temperature.

25. An exhaust system according to claim 24, wherein the second temperature is from 175-600°C, preferably from 250-450°C and most preferably from 300-400°C.
- 5 26. An exhaust system according to any of claims 22 to 25, wherein the first temperature is the same as the second temperature.
27. An exhaust system according to claim 19, wherein the control means, in use, interrupts the introduction of reducing agent through the first introducing means
10 when the first catalyst is below a third temperature.
28. An exhaust system according to claim 27, wherein the third temperature is from 75-200°C, preferably from 100-175°C and most preferably from 125-160°C.
- 15 29. An exhaust system according to claim 19, wherein the control means, in use, interrupts the introduction of reducing agent into the exhaust gas through the second introducing means when the second catalyst is above a fourth temperature.
30. An exhaust system according to claim 29, wherein the fourth temperature is 250-
20 600°C, preferably 450-600°C and most preferably 600°C and above.
31. An exhaust system according to any of claims 16 to 30, wherein the filter comprises an oxidation catalyst, optionally selected from at least one of a platinum group metal, a cerium component and a zirconium component.
- 25 32. An exhaust system according to any of claims 16 to 30, further comprising a catalyst capable of oxidising NO to NO₂ disposed upstream of the filter.
- 30 33. An exhaust system according to any of claims 16 to 32, further comprising a further catalyst capable of selectively catalysing the reduction of NO_x with a reducing agent disposed downstream of the filter.

34. A method of reducing NO_x in an exhaust gas flowing in an exhaust system of an internal combustion engine following cold-start, which exhaust system comprising a catalyst capable of selectively catalysing the reduction of NO_x with a reducing agent, which catalyst having a light off temperature for the reaction and being capable of adsorbing the reducing agent at below the light off temperature, which method comprising contacting the catalyst with a precursor of the reducing agent after engine key-off, adsorbing the precursor, or the reducing agent derived therefrom, on the catalyst between key-off and start up and reducing NO_x in exhaust gas contacting the catalyst following start up.
35. A method according to claim 34, wherein the light off temperature is in the range 100°C to 300°C.
36. A method according to claim 35, wherein the light off temperature is from 150°C to 250°C.
37. An exhaust system for an internal combustion engine, which system comprising a catalyst capable of selectively catalysing the reduction of NO_x with a reducing agent, which catalyst having a light off temperature for the reaction and being capable of adsorbing the reducing agent or a precursor thereof at below the light off temperature and means for contacting the catalyst with a precursor of the reducing agent after key-off whereby the precursor, or the reducing agent derived therefrom, is capable of adsorbing on the catalyst between key-off and start up.
38. An exhaust system according to claim 37, further comprising means for controlling the supply of the precursor to the catalyst.
39. A method of making ammonia and/or partially reduced nitrogen species for reducing NO_x in an exhaust gas of a lean burn internal combustion engine, which method comprising passing a hydrocarbon and a lean exhaust gas over a reforming catalyst.
40. An exhaust system for a lean burn internal combustion engine which system comprising means for contacting a reforming catalyst with a hydrocarbon, means for

contacting the reforming catalyst with at least a portion of a lean exhaust gas exhausted from an engine thereby to generate a reformat comprising ammonia and/or partially reduced nitrogen species with the hydrocarbon, a catalyst for selectively catalysing the reduction of NO_x with a reducing agent, and means for
5 contacting the SCR catalyst with the reformat.

41. An exhaust system for a lean burn internal combustion engine according to any of claims 16 to 33 or 37, which system further comprising means for contacting a reforming catalyst with a hydrocarbon, means for contacting the reforming catalyst
10 with at least a portion of a lean exhaust gas exhausted from an engine thereby to generate a reformat with the hydrocarbon, and means for contacting the second SCR catalyst with the reformat.

42. A method or system according to claims 39, 40 or 41, wherein the hydrocarbon is the
15 fuel that powers the engine.

43. A system according to claim 40, 41 or 42, wherein the exhaust gas is carried in an exhaust conduit, the reforming catalyst is disposed in the conduit and the means for contacting the reforming catalyst with a hydrocarbon is an injector disposed upstream
20 of the reforming catalyst.

44. A system according to claim 40, 41 or 42, wherein a portion of the exhaust gas is removed from the exhaust gas stream and directed to the reforming catalyst and the resulting reformat is reintroduced to the exhaust gas upstream of the SCR catalyst.
25

45. A method or system according to any preceding claim, wherein the reducing agent is a NO_x specific reactant.

46. A method or system according to claim 45, wherein the reducing agent is a
30 nitrogenous compound.

47. A method or system according to claim 46, wherein the nitrogenous compound is a nitrogen hydride.

48. A method or system according to claim 47, wherein the nitrogen hydride is ammonia or hydrazine
- 5 49. A method or system according to any of claims 1 to 38, wherein the reducing agent precursor is a precursor of a reducing agent according to any of claims 45 to 48.
50. A method or system according to claim 49, wherein the reducing agent is ammonia and the precursor is urea or ammonium carbamate.
- 10 51. A method or system according to claim 50, wherein the urea is an aqueous solution or a solid.
52. A method or system according to claim 51, wherein the aqueous urea solution is a eutectic mixture.
- 15 53. A method or system according to claim 51 or 52, wherein the aqueous urea solution includes additives to reduce the crystallisation temperature.
- 20 54. A method or system according to claim 45 or 46, wherein the reducing agent is obtained by reacting a hydrocarbon and lean exhaust gas over a reforming catalyst.
55. A method or system according to claim 54, wherein the reducing agent is at least one of ammonia, a nitrile, an amine, an oxime or an isocyanate.
- 25 56. A method or system according to any preceding claim, wherein the or each catalyst comprises a platinum group metal (PGM), preferably Pt.
57. A method or system according to any of claims 1 to 55, wherein the or each SCR catalyst comprises a base metal, preferably iron, cerium, copper or vanadium.
- 30 58. A method or system according to claim 57, wherein the or each catalyst further comprises at least one of Mo and W.

59. A method or system according to claim 57 or 58, wherein the base metal is supported.
- 5 60. A method or system according to claim 59, wherein the base metal support is at least one of alumina, titania, silica, silica-alumina, ceria, zirconia or a zeolite or a mixture or mixed oxide of any two or more thereof, preferably TiO_2 .
61. A method or system according to any preceding claim, wherein the or each catalyst is
10 not $\text{La/Cs/V}_2\text{O}_5$ or Pt/MgO .
62. A method or system according to any preceding claim, wherein the catalyst comprises a zeolite.
- 15 63. A method or system according to according to claim 62, wherein the zeolite is ZSM-5, mordenite, gamma-zeolite or beta-zeolite.
64. A method or system according to claim 62 or 63, wherein the zeolite comprises at least one metal or is metallised with at least one metal.
20
65. A method or system according to claim 64, wherein the at least one metal is selected from Cu, Ce, Fe or Pt or any two or more thereof.
66. A method or system according to claim 62, 63, 64, or 65, wherein the zeolite is ion-
25 exchanged or impregnated.
67. A system according to any of claims 40 to 44, wherein the reforming catalyst comprises a PGM or Ni.
- 30 68. A system according to claim 67, wherein the PGM is Rh, Pt or Rh-Pt.

69. A system according to claim 67 or 68, wherein the reforming catalyst comprises a support selected from the group consisting of alumina, titania, ceria, zirconia, silica, silica-alumina and mixtures and mixed oxides containing any two or more thereof.
- 5 70. A method or system according to any preceding claim, wherein the internal combustion (IC) engine is a lean burn engine.
71. A method or system according to claim 70, wherein the IC engine is a diesel engine.
- 10 72. A method or system according to claim 71, wherein the diesel engine is a heavy-duty diesel engine.
73. A method or system according to claim 70, wherein the IC engine is a gasoline engine, especially a gasoline direct injection (GDI) engine.

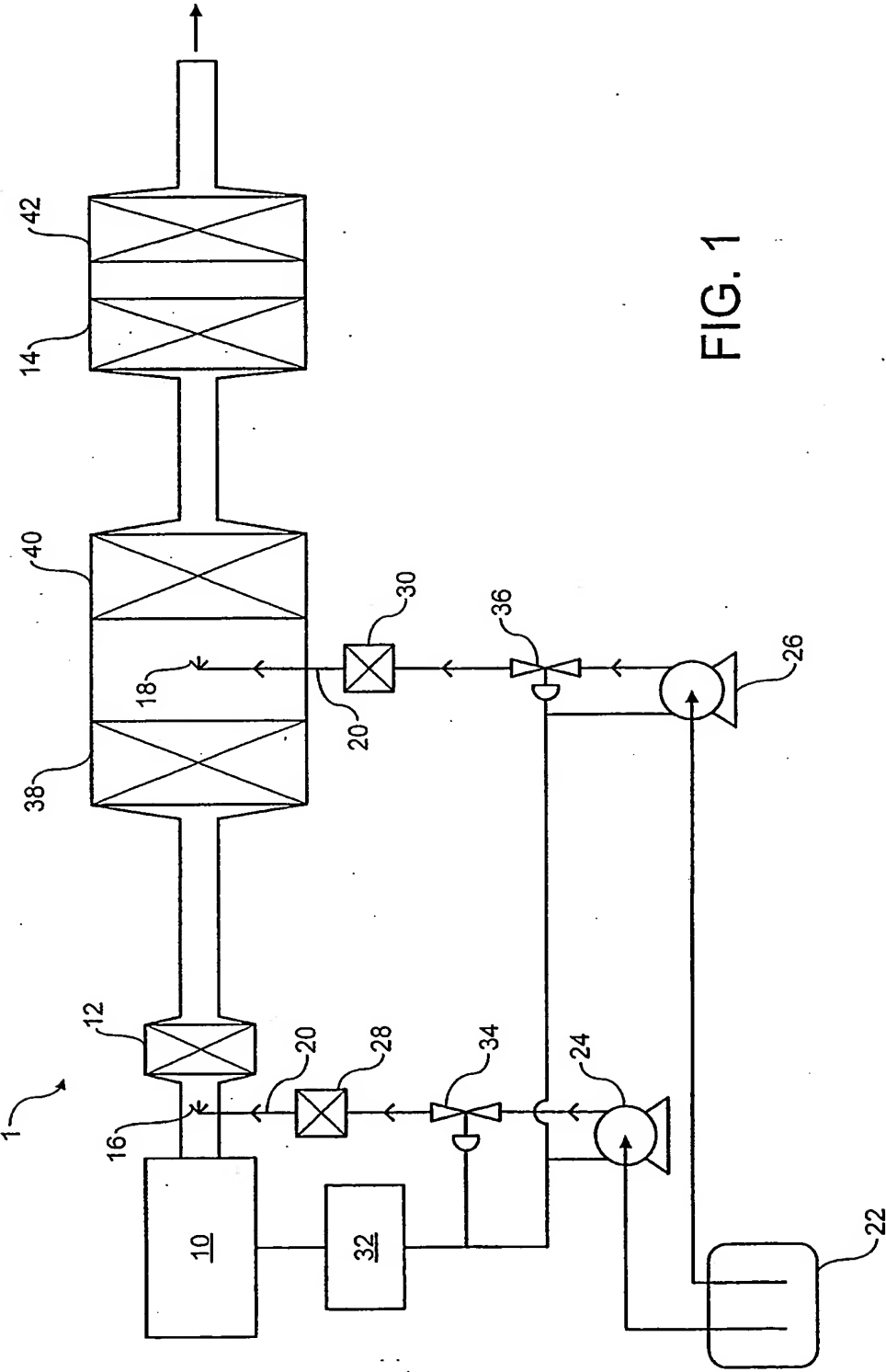
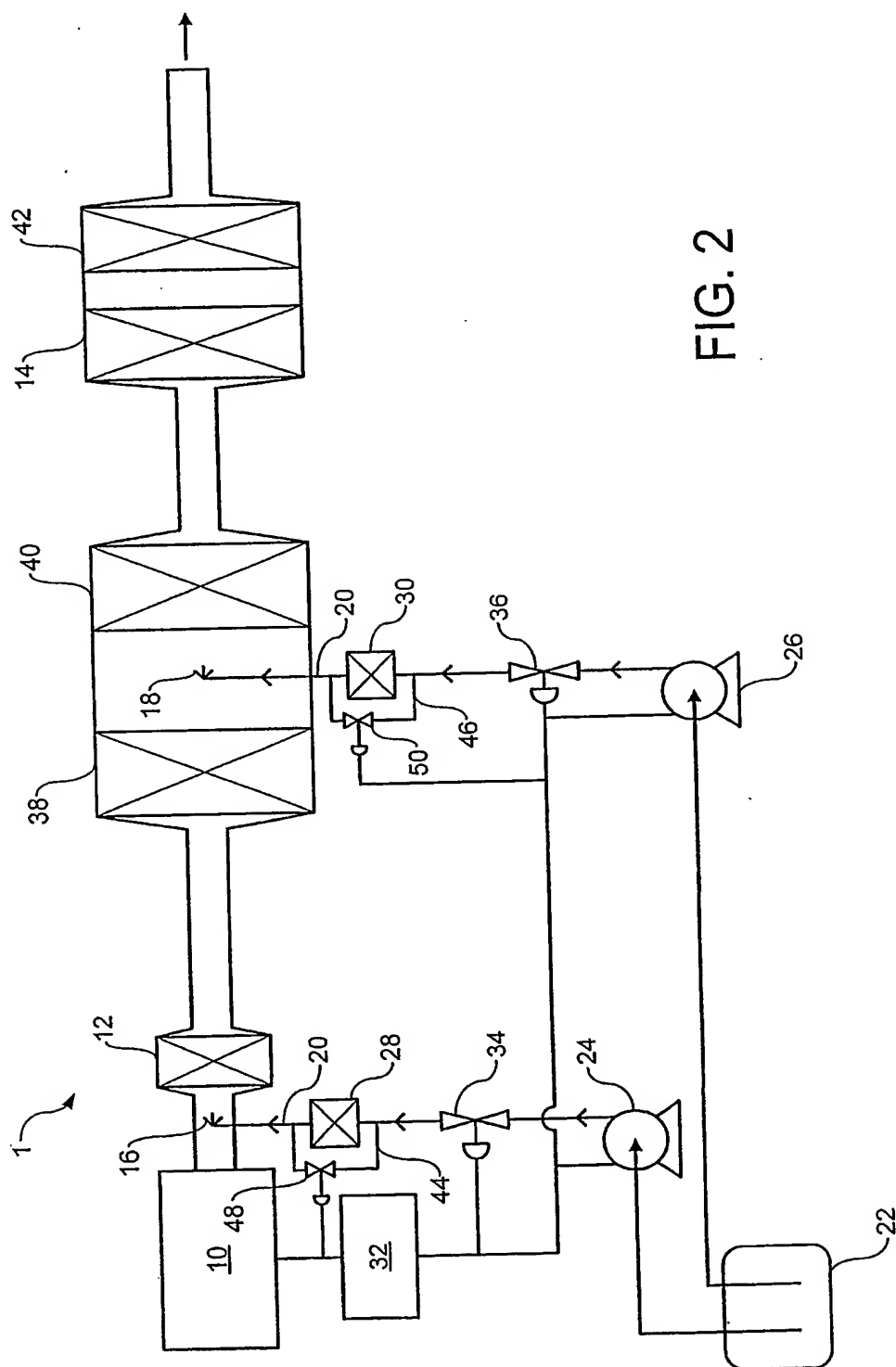


FIG. 1



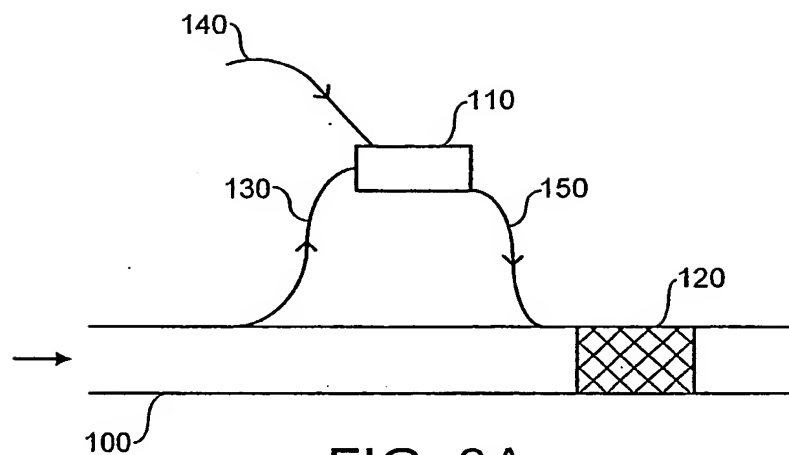


FIG. 3A

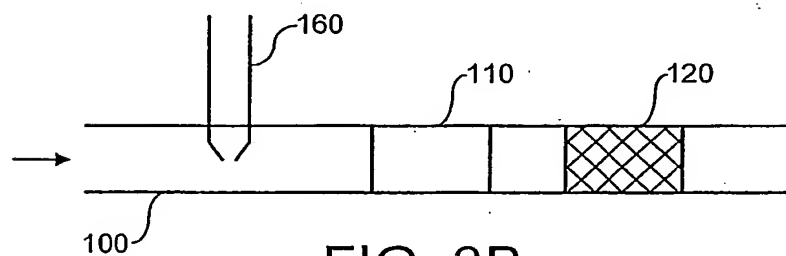


FIG. 3B

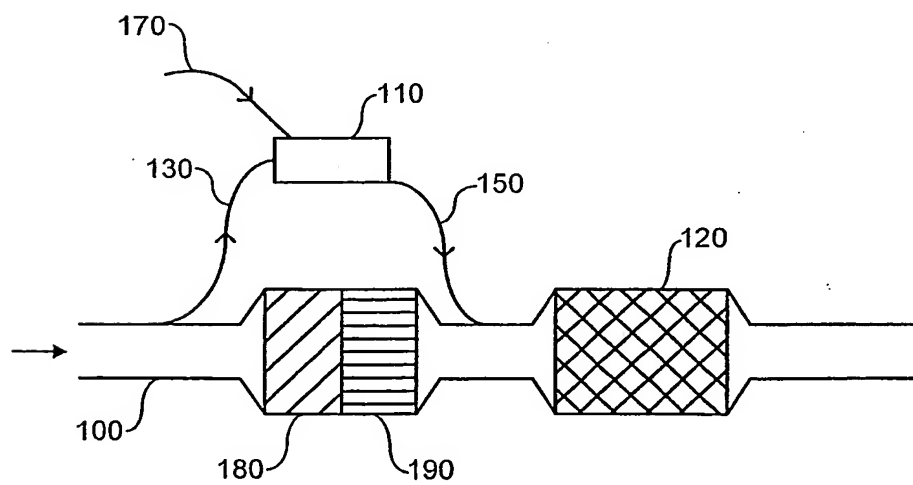
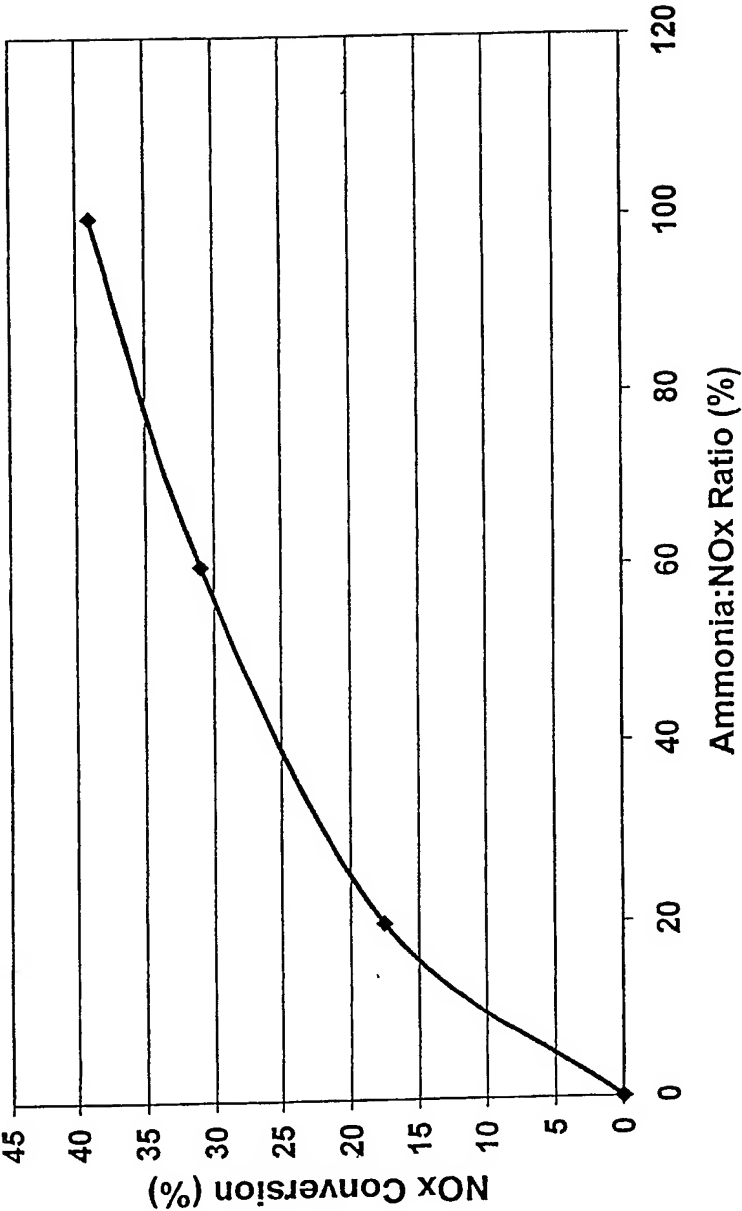


FIG. 3C

FIG. 4.



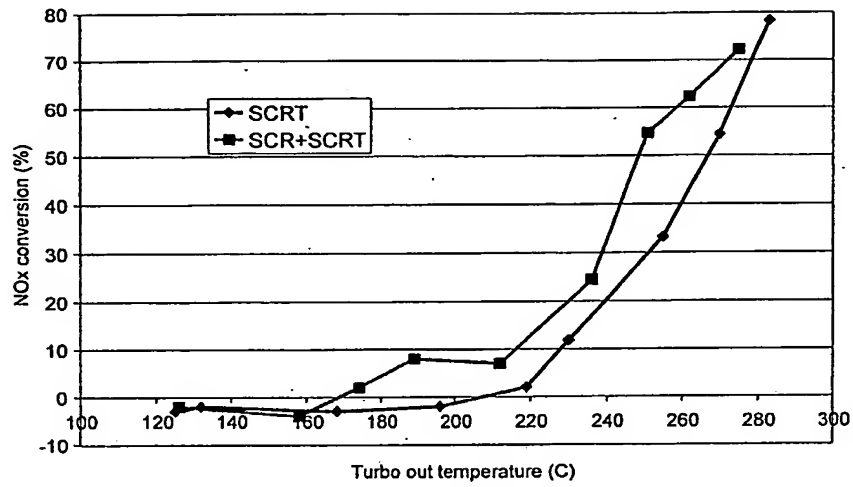


FIG. 5

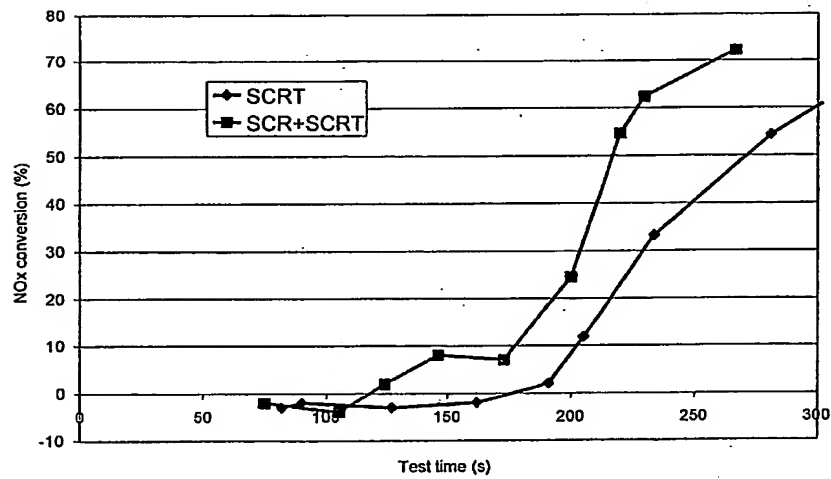


FIG. 6

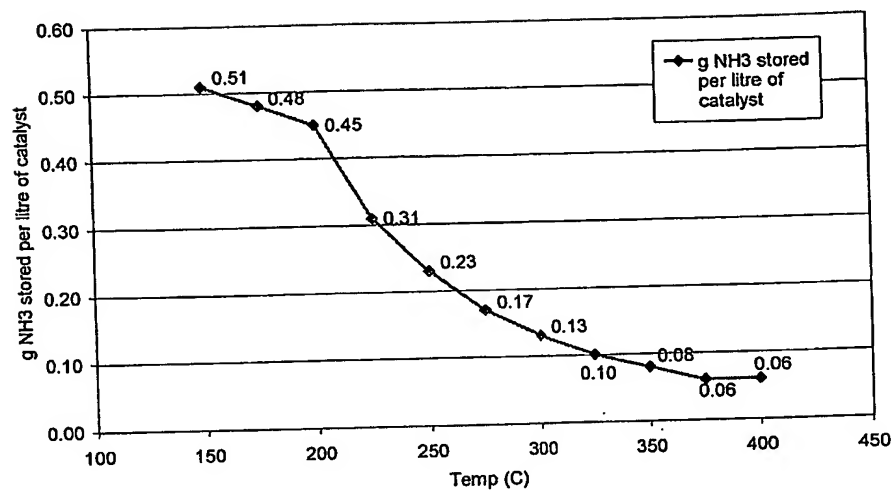


FIG. 7

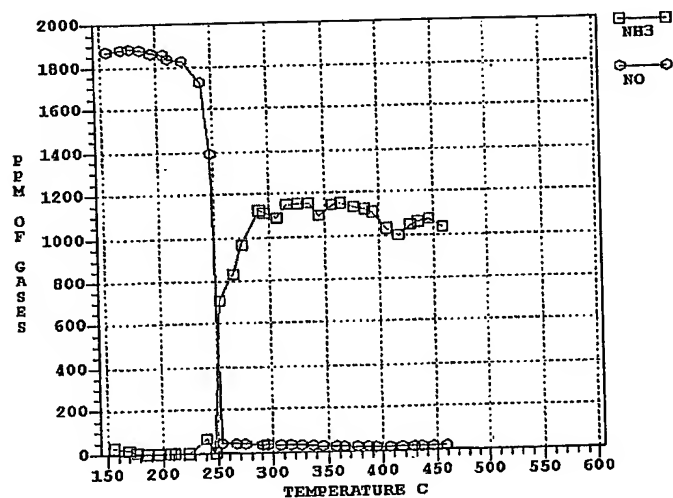


FIG. 8

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
3 July 2003 (03.07.2003)

PCT

(10) International Publication Number
WO 03/054364 A3

(51) International Patent Classification⁷: F01N 3/035,
3/20, 3/023, B01D 53/94, 53/90

(21) International Application Number: PCT/GB02/05839

(22) International Filing Date:
20 December 2002 (20.12.2002)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
0130474.0 20 December 2001 (20.12.2001) GB
0206888.0 25 March 2002 (25.03.2002) GB

(71) Applicant (for all designated States except US): JOHN-
SON MATTHEY PUBLIC LIMITED COMPANY
[GB/GB]; 2-4 Cockspur Street, Trafalgar Square, London
SW1 5BQ (GB).

(72) Inventors; and

(75) Inventors/Applicants (for US only): BLAKEMAN,
Philip, Gerald [GB/GB]; 11 Argyle Street, Cambridge

CB1 3LR (GB). TWIGG, Martin, Vincent [GB/GB];
108 Ermine Street, Caxton, Cambridge CB3 8PQ (GB).
WALKER, Andrew, Peter [GB/GB]; 57 Bramley Av-
enue, Melbourn, Royston SG8 6GB (GB). GOLUNSKI,
Stanislaw, Edmund [GB/GB]; 2 Widmore Lane, Sonning
Common, Reading RG4 9RR (GB). CHANDLER, Guy,
Richard [GB/GB]; 48 Harlton Road, Little Eversden,
Cambridge CB3 7HB (GB).

(74) Agent: NUNN, Andrew, Dominic; Johnson Matthey
Technology Centre, Blounts Court, Sonning Common,
Reading RG4 9NH (GB).

(81) Designated States (national): JP, US, ZA.

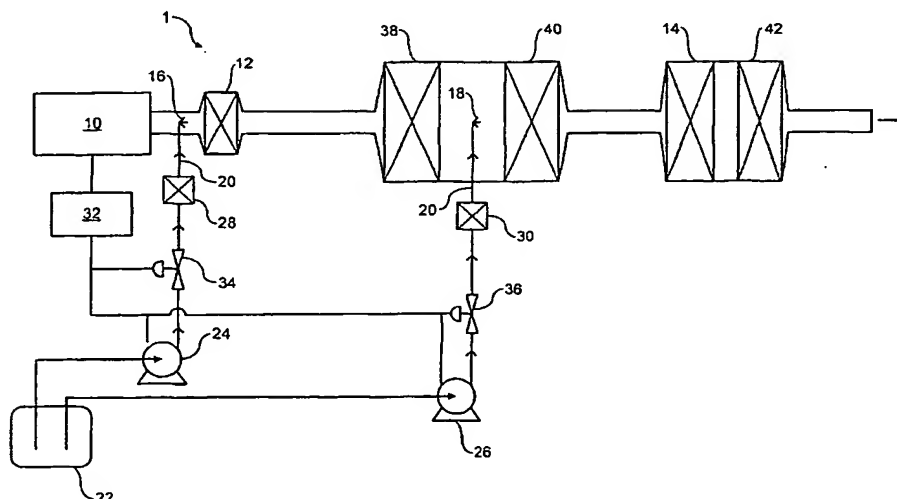
(84) Designated States (regional): European patent (AT, BE,
BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, IE, IT,
LU, MC, NL, PT, SE, SI, SK, TR).

Published:

- with international search report
- before the expiration of the time limit for amending the
claims and to be republished in the event of receipt of
amendments

[Continued on next page]

(54) Title: METHOD AND APPARATUS FOR FILTERING PARTICULATE MATTER AND SELECTIVE CATALYTIC RE-
DUCTION OF NO_x



(57) Abstract: A method of selectively catalysing the reduction of NO_x in an exhaust gas flowing in an exhaust system of an internal combustion engine comprising a filter (40) for particulate matter comprising a catalyst capable of selectively catalysing the reduction of NO_x with a reducing agent, which method comprising introducing a reducing agent, or a precursor thereof, into the exhaust gas and contacting the resulting gas with the filter (40).



WO 03/054364 A3

WO 03/054364 A3



(88) Date of publication of the international search report:
28 August 2003

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/GB 02/05839

A. CLASSIFICATION OF SUBJECT MATTER IPC 7 F01N3/035 F01N3/20 F01N3/023 B01D53/94 B01D53/90		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) IPC 7 F01N B01D		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practical, search terms used) WPI Data, PAJ, EPO-Internal		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P, X	WO 01 96717 A (CHAPMAN KENNETH HAZEL ; JOHNSON MATTHEY PLC (GB); WILKINS ANTHONY J) 20 December 2001 (2001-12-20) cited in the application page 11, line 28 -page 12, line 3; figures 1-3	1, 15, 16, 19-33, 45-73
P, X	EP 1 174 599 A (PUREM ABGASSYSTEME GMBH & CO K) 23 January 2002 (2002-01-23) column 1, paragraph 2 - paragraph 3 column 5, paragraph 22 -column 6, paragraph 23; claims; figures 4-6 --- -/-	1, 16
<input checked="" type="checkbox"/> Further documents are listed in the continuation of box C.		
<input checked="" type="checkbox"/> Patent family members are listed in annex.		
* Special categories of cited documents : "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the International filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the International filing date but later than the priority date claimed "T" later document published after the International filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "Z" document member of the same patent family		
Date of the actual completion of the International search 27 June 2003		Date of mailing of the International search report 30.07.03
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016		Authorized officer Eijkenboom, A

INTERNATIONAL SEARCH REPORT

national application No.
PCT/GB 02/05839

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:
3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 8.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

1. ☒ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest.

☒ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. Claims: 1-33,45-73 (part)

A method and system for selectively catalysing the reduction of NOx in exhaust gas of an internal combustion engine, comprising introducing a reducing agent or its precursor into the exhaust gas and contacting the resulting gas with a filter for particulate matter comprising a catalyst capable of selective reduction of NOx.

2. Claims: 34-38, 45-73 (part)

Method and system for reducing NOx in an exhaust gas from an internal combustion engine following cold-start, comprising introducing a reducing agent precursor into the exhaust gas and contacting the resulting gas with a catalyst capable of selectively catalysing the reduction of NOx, whereby the reducing agent or precursor is adsorbed on the catalyst below its "light off temperature"

3. Claims: 39-44, 45-73 (part)

Method and system for making ammonia and/or partially reduced nitrogen species for reducing NOx in an exhaust gas of a lean burn internal combustion engine, comprising passing a hydrocarbon and an exhaust gas over a reforming catalyst. The system further comprises a SCR catalyst and means for contacting the latter with the reformat.

INTERNATIONAL SEARCH REPORT

 International Application No
 PCT/GB 02/05839

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 01 12320 A (JOHNSON MATTHEY PLC ;WILKINS ANTHONY JOHN JOSEPH (GB); BRISLEY ROB) 22 February 2001 (2001-02-22) page 8, line 30 -page 9, line 28; claims; figure	1, 16, 31-33, 45-73
Y		2-15, 17-30
X	WO 01 80977 A (BOSCH GMBH. ROBERT ;MAHR BERND (DE)) 1 November 2001 (2001-11-01) page 11, line 15-17; figures 1-3	1, 16, 31-33, 45-73
X	DE 198 34 541 A (BUCK ALFRED) 3 February 2000 (2000-02-03) column 1, line 66 -column 2, line 7; figure 1'	1, 16, 19, 45-73
X	WO 00 28196 A (CERYX INC ;EDGAR BRADLEY L (US); PAGE DORRIAH L (US); MACDONALD RO) 18 May 2000 (2000-05-18) page 9, line 4 - line 6; figure 1	1, 16
Y	US 6 314 722 B1 (MATROS YURII SH ET AL) 13 November 2001 (2001-11-13) column 10, line 30 - line 55; figure 5	2-15, 17-30
A	PATENT ABSTRACTS OF JAPAN vol. 015, no. 336 (M-1151), 26 August 1991 (1991-08-26) & JP 03 130522 A (MITSUBISHI HEAVY IND LTD), 4 June 1991 (1991-06-04) abstract	1-33
A	GB 2 333 471 A (JOHNSON MATTHEY PLC) 28 July 1999 (1999-07-28) the whole document	1-33
X	WO 99 55446 A (GOERSMANN CLAUS FRIEDRICH ;JOHNSON MATTHEY PLC (GB); SELF VALERIE) 4 November 1999 (1999-11-04) cited in the application page 3, line 4 -page 4, line 20; claims page 3, line 20 - line 21	34-38, 45-73
X	EP 0 773 354 A (TOYOTA MOTOR CO LTD) 14 May 1997 (1997-05-14) column 8, line 26 -column 9, line 13; figures 4A, 4B	39, 40, 45-73
X	WO 00 76637 A (NISSELROOIJ PETRUS FRANCISCUS ;GASTEC NV (NL); BOUWMAN WILLEM HEND) 21 December 2000 (2000-12-21) page 4, line 13 -page 5, line 10; claims page 6, line 28 - line 35	39, 40, 45-73

INTERNATIONAL SEARCH REPORT

 Int l Application No
 PCT/GB 02/05839

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
WO 0196717	A	20-12-2001	EP 1290318 A1 WQ 0196717 A1	12-03-2003 20-12-2001
EP 1174599	A	23-01-2002	DE 10035544 A1 EP 1174599 A1 US 2002021988 A1	31-01-2002 23-01-2002 21-02-2002
WO 0112320	A	22-02-2001	EP 1133355 A1 WO 0112320 A1	19-09-2001 22-02-2001
WO 0180977	A	01-11-2001	DE 10020555 A1 WO 0180977 A1	31-10-2001 01-11-2001
DE 19834541	A	03-02-2000	DE 19834541 A1 AU 6187699 A WO 0008314 A1	03-02-2000 28-02-2000 17-02-2000
WO 0028196	A	18-05-2000	AU 1342200 A CA 2350027 A1 EP 1149232 A1 JP 2002529649 T WO 0028196 A1	29-05-2000 18-05-2000 31-10-2001 10-09-2002 18-05-2000
US 6314722	B1	13-11-2001	NONE	
JP 03130522	A	04-06-1991	NONE	
GB 2333471	A	28-07-1999	NONE	
WO 9955446	A	04-11-1999	AU 741813 B2 AU 3616499 A CA 2329994 A1 CN 1306455 T EP 1083979 A1 WO 9955446 A1 JP 2002513110 T PL 343689 A1 TW 469163 B	13-12-2001 16-11-1999 04-11-1999 01-08-2001 21-03-2001 04-11-1999 08-05-2002 27-08-2001 21-12-2001
EP 0773354	A	14-05-1997	JP 9133032 A DE 69616235 D1 DE 69616235 T2 EP 0773354 A1 US 5782087 A	20-05-1997 29-11-2001 27-06-2002 14-05-1997 21-07-1998
WO 0076637	A	21-12-2000	NL 1012296 C2 AU 5579600 A CA 2374647 A1 CN 1355721 T EP 1204458 A1 WO 0076637 A1	12-12-2000 02-01-2001 21-12-2000 26-06-2002 15-05-2002 21-12-2000

THIS PAGE BLANK (USPTO)